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Application of liposomes in textile dyeing

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ABSTRACT

Phosphatidylcholine liposomes were applied to wool dyeing with acid milling dyes, with azo or anthraquinone disperse dyes and with 1:2 metal complex dyes in all cases with and without cholesterol on the bilayer. Given the valuable effect of synthetic and natural double tailed surfactants on polyester dyeing and the significant improvement achieved in wool dyeing, recent results obtained on the dyeing of wool/polyester blends using liposomes are also presented.

LUV and MLV liposome suspensions at pH 5.5 were physicochemically stable during the dyeing process for both dyes studied, the bilayer lipid concentration ranging from 0.5 to 4.0 mM. The presence of increasing amounts of CH in liposomes enhanced the stability of these structures for both the particle size distribution and the polydispersity index.

Despite the inhibition of dye exhaustion on untreated wool fabrics, directly dependent on both the liposome lipid concentration and the structure of liposomes, the increasing concentrations of lipids in the bilayers enhanced the percentage of bonded dye in the fibres. This tendency was also observed when the CH concentration in the bilayers was increased. Therfore, a new method of wool dyeing by means of liposomes may be considered suitable for modulating the dye exhaustion of commercial milling acid dyes, disperse dyes and metal complex dyes, thereby increasing the dye bonding in untreated wool fibres.

In the dyeing of polyester with disperse dyes, the carrier character of liposomes was demonstrated. Dye exhaustion and fixation were directly dependent on the amount of fibre in the dyebath regardless of the dye concentration and temperature. Liposomes action was valued in blends of polyester/wool with disperse dyes under optimum conditions for polyester dyeing. In this case dyebath exhaustion depended on the dye concentration, attaining higher exhaustion levels at higher temperatures and with only light shades. The dye bonded on polyester and wool were higher with liposome dyeing than with commercial carrier dyeing. New strategies for wool/polyester blend dyeing could be devised using more specific biomimetic systems with a vesicular character suited to textile applications.

INTRODUCTION

Liposomes can be regarded as an excellent model for cell membranes and can also be employed in controlled delivery systems for therapeutic agents. In the last decade, these vesicles have aroused a great deal of interest in the pharmaceutical, food and cosmetic fields. Eventhough they have not been industrially applied in the field of textiles, some studies have been carried out at laboratory level which could envisage a new use for these vesicles in textile dyeing.

Attempts to apply vesicles to textile dyeing have been carried out by several authors. Barni et al. (1) applied to the dyeing of polyester, cationic and anionic double tailed surfactants, such as di-dodecyl-dimethylammonium bromide (DDDAB) or chloride (DDDAC) and di-hexadecylphosphate (DHP), suitable for the preparation of synthetic vesicles. The disperse dye used belongs to the diethylamino-azobenzene series and excellent results were obtained for dyebath exhaustion and uniformity of coloration.

In the same line Kim et al. also used DDDAB and other di-alkyl derivatives such as di-decyl or di-

hexadecyl-dimethylammonium bromide, on disperse dyeing of nylon (3) and polyester fibres (4). The dyeing behaviour of 1,4-diaminoantraquinone (1,4-DAA) on nylon 6 and polyester fibres in the presence of these double tailed surfactants which are known to form liposomes were found to increase both the saturation value and the dyeing rate.

Carrión applied soya lecithin, a double tailed natural phospholipid, as a stable microemulsifer for a volatile carrier such as dichloromethane at low temperature dyeing of polyester (2). The kinetics of this dyeing system was determined as a function of temperature with various disperse dyes at different molecular weights. In general, dyes with lower molecular weight had a faster dyeing rate and activation energies were similar to those achieved in traditional dyeing with a carrier.

Egg phosphatidylcholine liposomes have been demonstrated to be effective for chlorination (5,6) and dyeing of wool (7-14). The fact that the bilayer structuration of the lipids from the "Cell Membrane Complex" from wool is similar to that of the liposomes togetter with the important role played by this morphological fraction of the fibre in the processing of chemicals into fibres has enabled liposomes to be used as carriers in wool finishing.

In this regard, liposomes composed of pure phosphatidylcholine (5) or containing lipids present in the CMC such as cholesterol (6), have been used as vehicles for aqueous chlorine solutions in wool chlorination processes. These applications result in an improvement in both the regularity and the homogeneity of these oxidative treatments, minimizing wool degradation and improving the subsequent treatments in wool processing.

In the same way phosphatidylcholine liposomes have been applied to wool dyeing with acid milling dyes (7-10), with azo or anthraquinone disperse dyes (11-14) and recently with 1:2 metal complex dyes (15,16) in all cases with and without cholesterol in the bilayer.

Given the aforementioned valuable effect of synthetic and natural double tailed surfactants on the polyester dyeing and the significant improvement achieved in wool dyeing, we present in this review recent results (17) obtained from dyeing of wool/polyester blends using liposomes.

METHODOLOGY

A. Materials

Botany wool fabrics knitted from R64/2 tex (count 2/28) yarns were used (7-16). Samples were soxhlet extracted for 2 hours with methylene chloride and rinsed with water purified by the Milli-Ro system (Millipore) and dried at room temperature. Flat woven polyester fabrics were also used (17).

Phosphatidylcholine (PC) was purified from egg lecithin (Merck) according to the method of Singleton (18) and shown to be pure by thin-layer chromatography (TLC). Cholesterol (CH) was purchased from Sigma Chemical Co. (St. Louis, MO).

Commercial liposomes Ecotrans-100-H supplied by Transtechnics (Barcelona) are small unilamellar vesicles of an approximate size of 100 nm, made up of 5% of soya lecithin (containing 93-97% of phosphatidilcholine), water solution of NaCl 0.9%, ethanol and Dl-α-tocopherol (as antioxidant) (17).

Triton X-100 (octylphenol ethoxylated with 10 units of ethylene oxide and an active matter of 100%) was supplied by Tenneco,S.A. (Spain). Polycarbonate membranes of 400 nm and 800 nm, and membrane holders used for liposome extrusion were purchased from Nucleopore (Pleasanton, CA).

Dyes applied to wool were the following: Polar Red B, CI Acid Red 249 (7,10) and Polar Blue G, CI Acid Blue 90 (7-10) Ciba-Geigy milling acid dyes; CI Disperse Orange 1 (11,14) Sigma Chemical Co. azo-disperse dye; Oracetblau 2R, CI Disperse Violet 1 (12,13) Merck antraquinone disperse dye; Yellow Irgalan 2GL KWL, CI Acid Yellow 129 (15,16) Ciba-Geigy 1:2 metal complex dye. Dye applied to polyester was the following: Terasil Yellow 4G, CI Disperse Yellow 211 (17) Ciba-Geigy azo-disperse dye.

B. Preparation, characterization and stability of liposomes containing dyes

The liposomes used for these studies were large unilamellar vesicles (LUV) and multilamellar vesicles (MLV) of a variety of lipid compositions. The conditions of each preparation are outlined below.

1. LUV

Large unilamellar vesicle suspensions of a defined size (400 nm) at different lipid concentrations (from 0.5 to 4.0 mM) to the PC/CH mixtures (from 10:0 to 8:2 molar ratios) containing in each case the dye to be studied were prepared by reverse phase evaporation under nitrogen atmosphere as described by Paternostre and Rigaud (19,20). This procedure was essentially derived from the general procedure of Szoka and Papahadjopoulos (21). After preparation the resulting liposome suspensions containing dyestuff were left to equilibrate for 15 minutes and immediately applied to the wool dyeing processes (8).

2. MLV

Multilamellar vesicle liposomes of a defined size (400 nm) containing in each case the dye to be studied in the same range of lipid concentrations and also including CH in the same molar ratios were prepared following a method described by Bangham (22). The resulting milky suspensions were vortexed for 5 minutes and sonicated for 15 minutes at 30°C and 75 W (Labsonic 1510 B. Braun). Likewise, the vesicle suspensions were sequentially extruded through 800 and 400 polycarbonate membranes to obtain a uniform size distribution.

Encapsulation Efficiency

The percentages of encapsulated dye in liposomes (expressed in % volume) were determined using a spectrophotometric method. After preparation, liposome suspensions were cleared of unencapsulated dye by separation through Sephadex G-50 medium resin (Pharmacia Sweden) column chromatography (23). Then, the concentration of entrapped dye was evaluated by spectrophotometry after the solubilization of the supernatant lipid bilayers by addition of Triton X-100 (24).

Physical Stability

The aggregation state of the vesicles was estimated as a measure of the physical stability of the liposome suspensions. This was done by monitoring the variation of the mean vesicle size distribution of liposome suspensions as a function of time. This parameter together with the polydispersity indexes of the liposome suspension was determined using a photon correlator spectrometer (Malvern Autosizer 4700c PS/MV). Vesicle size distributions were made by particle number measurements. Samples were adjusted to the appropriate concentration range with a dyebath solution. Measurements were made at 25°C with a detection angle of 90°.

C. Dyeing Procedures

Wool knitted samples (7-16) were treated with LUV or MLV liposome suspensions freshly prepared containing the coresponding dye at different PC:CH molar ratios (from 10:0 to 8:2); the lipid concentration of bilayers ranging from 0.25 to 4.0 mM. The dye was applied from 0.1 to 2% (o.w.f.) with a 5% sodium sulphate solution, acetic acid to pH 5.5 and liquor ratio of 60:1.

Dyeing was initiated at 50°C and the temperature was raised by 0.9 °C/ min to 90°C. Dyeing was continued for 120 min. Next, samples were rinsed with water for 10 min and dried at room temperature. Laboratory dyeing was carried out in a Multi-Mat dyeing machine (Renigal).

Polyester samples or polyester/wool blends (17) were treated with the commercial liposomes or with conventional auxiliaries of commercial dyeing as follows. The liposome dyebaths were prepared at room temperature with liposomes (0.1 to 1% of PC owf), disperse dye (0.2 to 3% owf) and acetic acid (2.5% owf). Conventional dyebaths were prepared at room temperature with Optinol BD as a carrier from Yorkshire (1.5g/L), Tanacid TAB as a dyeing auxiliary from Sybron (0.8 g/L) and disperse dye (0.2 to 3% owf).

Dyeing was initiated at room temperature and the temperature was raised by 2 °C/min to 80°C and then by 1°C/min until the maximum (100°,105°,110° or 120°) remaining at this temperature for 45min. Next, samples were rinsed with water, then squeezed in a laboratory foulard, and dried in an oven at 100°C during 10 min. Laboratory dyeing was carried out in a Tin-Control Tacaltex 90S dyeing machine with tubes of 150mL with a hermetical cover.

Dyebath exhaustion was determined using a Shimadzu UV-265FW spectrophotometer. Liposome aliquots (0.5 ml) were periodically added to quartz cuvettes filled with 2 ml of aqueous solution of Triton X-100 (10 g/l), supplemented with sodium sulphate (5%) and acetic acid at pH 5.5. The interaction between the nonionic surfactant Triton X-100 and liposome structures resulted in a solubilization of lipid vesicles

via mixed micelle formation, turning the liposome suspensions into clear solutions.

The wavelength of maximum absorption of each dye used in this research does not change in the presence of the phospholipid-surfactant mixed micelles. A similar effect was observed when using liposomes containing CH in the bilayer in the range of PC:CH molar ratios from 10:0 to 8:2.

D. Dye Extractions of Samples

After the dyeing process, the superficial dye bonded on the wool fibers by nonpolar forces (hydrophobic interactions, van der Waals forces and hydrogen bonds) was extracted with pure ethanol at 25°C for 60 min (8). Subsequent extractions with ammonia solution (0.5% at 60°C for 15 minutes) stripped the dye diffused inside the fibre and bonded ionically (25a). The superficial dye bonded on the polyester fibres was extracted with acetone at 0°C for 4 min (17).

RESULTS AND DISCUSSION

A. Stability of Liposome Suspensions

LUV and MLV liposome suspensions containing the different dyes were treated under the same conditions as in the dyeing process but in the absence of wool and using the same lipid bilayer concentrations at different lipid compositions (PC:CH molar ratios from 10:0 to 8:2). There was a small decrease in the particle size distribution in the initial stage of the dyeing process in all cases. After 30 minutes, vesicle size increased slightly reaching maximum growth after approximately 100 minutes of dyeing (vesicle size about 430-435 mn), the polydispersity indexes remaining below 0.24 after treatment in all cases.

Increasing amounts of CH in liposomes enhanced the stability of these systems with respect to the aggregation, reducing both the mean particle size distribution and the polydispersity indexes during dyeing. This behaviour is in agreement with the results reported by Scherphof et al. in studies on liposome stability (26).

The chemical structure of dye and the type of vesicles used do not seem to affect the physical stability of the dye-liposome system. Furthermore, the mean vesicle size distribution and the polydispersity index were maintained at around 400 nm and below 0.24 respectively for more than 24 hours.

As a consequence, the LUV and MLV liposome suspensions including the studied milling acid dyes, disperse dyes and 1:2 metal complex dyes were physically stable during the dyeing process for the lipid concentration range and lipid compositions studied.

B. Encapsulation Efficiency and Dispersion Capacity of Liposomes

The relative concentrations of encapsulated dye in LUV and MLV liposomes in the two cases of acid milling dyes investigated were found to be different (7-10). The results obtained for Polar Blue G at different lipid compositions (PC:CH molar ratios 10:0 and 8:2) are plotted versus the bilayer lipid concentration (Fig. 1).

The encapsulation efficiency increased in direct proportion to the lipid concentration of liposomes for both lipid structures studied. Increasing amounts of CH in the bilayers slightly decreased the percentages of dye encapsulated in all cases. The higher encapsulation efficiency of the LUV suspensions (maximum value of about 25 % for 4.0 mM lipid concentration) could be explained by the

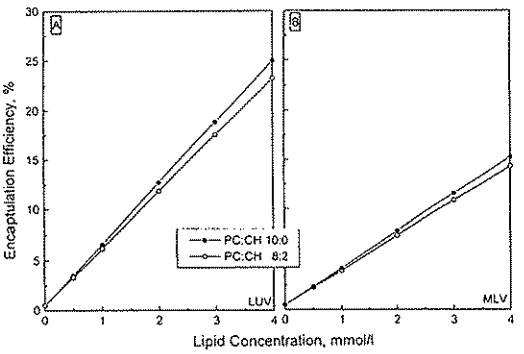

FIGURE 1. Percentages of encapsulation efficiency of LUV (A), and MLV (B), liposome suspensions containing Polar Blue G versus bilayer lipid concentration for PC:CH molar ratios 10:0 and 8:2.

unicompartmental architecture of these species whose vesicles show a higher internal volume (27).

The dispersion capacity of liposomes was determined for the disperse dyes studied (11-14). The maximum amounts of dyes dispersed with MLV liposomes were found to be directly proportional to the phospholipid concentration in bilayers over the concentration range studied. Variations in the total amounts of the two dispersed dye studied at different lipid compositions versus bilayer lipid concentration are shown (Fig. 2).

A linear dependence was established in all cases. The slope of the straight lines obtained represents the weight ratio between dye and lipid, K. The K values in the two cases decreased as the CH concentration in the bilayers increased (from 0.24 to 0.18 for the Disperse Violet 1, and from 0.30 to 0.26 for the Disperse Orange 1). In all cases it could be concluded that MLV liposomes clearly improved dispersion efficiency compared with conventional dispersing agents (25b).

C. Wool Dyeing Kinetics

Different kinetic studies of dye exhaustion of untreated wool samples for the aforementioned dyes via liposomes were performed to study the influence of different variables such as PC concentration, dye concentration, liposome structure (LUV,MLV), CH concentration, percentage of encapsulation, etc., to clarify the role of liposomes in wool dyeing.

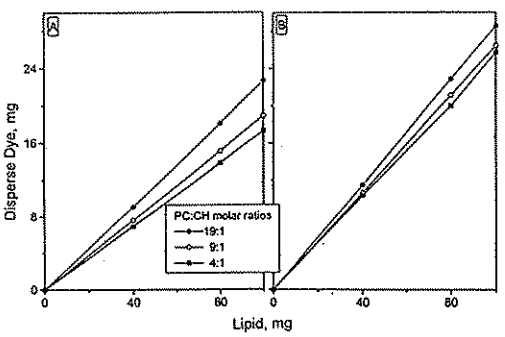

FIGURE 2. Maximum amounts of antraquinonic Disperse Violet 1 (A), and azobenzene disperse Orange 1 (B), dyes as a function of lipid concentration for three levels of CH in bilayers.

Influence of PC concentration

Kinetic studies of dye exhaustion of untreated wool samples in the presence of liposomes were carried out for all dyes studied varying the phospholipid concentration with the dye concentration remaining constant (7,8,10-15). Figure 3 shows two representative cases of dyeing kinetics with an acid milling dye, Polar Blue G and with a 1:2 metal complex dye Acid Yellow 129, via LUV liposomes mantaining constant the dye concentration (1% owf) and varying the PC concentration.

As can be seen, the use of liposomes as carriers in wool dyeing resulted in an inhibition of dye exhaustion for both dyes presented and this also applied to all the dyes studied. However, although in the case of Polar Blue G (also Polar Red B and Disperse Violet 1) this inhibition is directly related to the increase in phospholipid concentration, in the case of Acid Yellow 129 (also Disperse Orange 1) the dyebath exhaustion increases as the PC concentration in the bilayers rises reaching a maximum which again falls with the PC concentration.

Therefore, it can be concluded that for a constant dye concentration the dye exhaustion inhibition is directly related to the amount of liposomes present in the bath, reaching in some cases an optimum of maximum dye exahustion which should be determined.

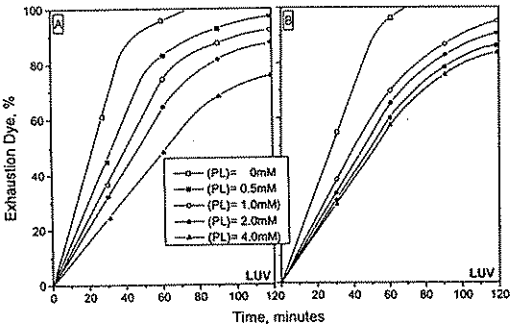

FIGURE 3. Exhaustion kinetics of (A) Polar Blue (7,10) and (B) 1:2 Metal complex dye (15) on untreated wool samples via LUV liposomes (at different PC concentrations) versus time.

Influence of dye concentration

The kinetics of dye exhaustion of different liposome systems was studied for disperse dyes, the lipid concentration remaining constant (1.0mmol/L), the dye concentration ranging from 0.2 to 1.0 mmol/L (Figure 4).

Interestingly, dye exhaustion rises as dye concentration in liposomes increases, reaching the highest values (79%) for 0.7mmol/L dye concentration for Disperse Orange 1, or (90.%) for 0.5mmol/L dye concentration for Disperse Violet 1. Increasing amounts of dye also result in decreased dye exhaustion in the range of the dye and lipid investigated.

On the basis of the last two sections, the importance of the dye/phospholipid molar ratios to obtain dyeing modulation at a maximum of dye exhaustion can be pointed out.

Influence of liposome structure

The higher encapsulation efficiency found for LUV suspensions should be reflected in the dyeing behaviour of the same dye with the two liposome structures studied. Results of measuring dye exhaustion for Polar Red B in dyeing via LUV and MLV liposomes are plotted in Figure 5.

The use of liposomes in dyeing results in an inhibition of dye exhaustion for both structures studied, the

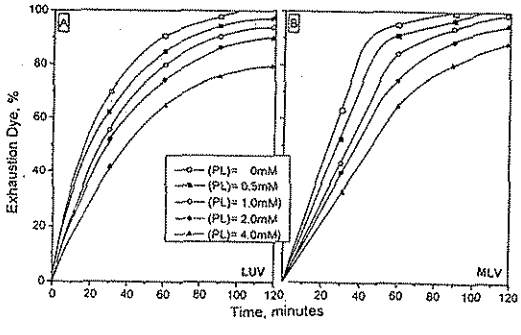

FIGURE 4. Exhaustion kinetics of (A) Disperse Orange 1 (11) and (B) Disperse Violet 1 (12) on untreated wool at different dye concentrations and constant phospholipid concentration (1.0 mmol/L)

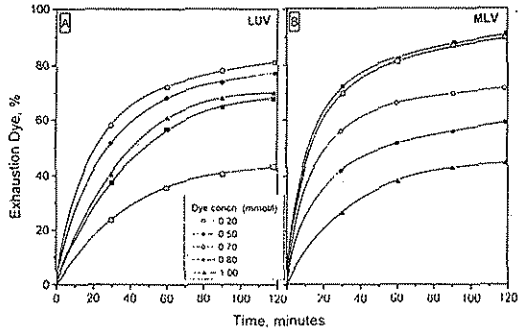

FIGURE 5. Exhaustion kinetics of polar red B dye (10) on untreated wool samples in dyeing via A) LUV and B) MLV liposomes (at different PC concentration) versus time.

effect being greater for LUV suspensions. The final dye exhaustion for 4mM/L lipid concentration was appoximately 77% for LUV and 83% for MLV liposome suspensions. Therefore, the higher inhibition of dye exhaustion of the LUV versus the MLV could probably be attributed to the higher encapsulation efficiency of the LUV structures.

Influence of CH concentration

As cholesterol is one of the main components of the internal lipids of wool (28), we studied the effect caused by including this component in lipid bilayers on wool dyeing. Accordingly, we investigated the dye exhaustion kinetics also for most of the dyes described via liposomes containing increasing amounts of CH in bilayers (9,10,13,14,16). The results obtained for two of them Polar Blue G (10) and Acid Yellow 129 are given in Figure 6.

In general, the marked inhibition of dyeing exhaustion versus dyeing in the absence of liposomes, more pronounced in A, is attributable to the use of the higher lipid bilayer concentration.

As regards to the influence of the molecular composition of liposomes, this inhibition was directly connected to the presence of CH in bilayers; i.e., the greater the CH concentration in the bilayers, the higher the inhibition of dye exhaustion in A and most of the other dyes studied (9,10,13,14). However, in B, the inhibition was inversely connected to the presence of CH in bilayers. Thus, the higher the

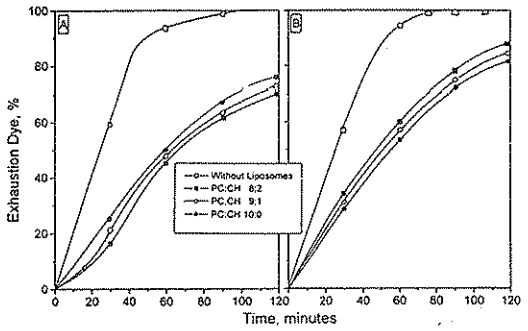

FIGURE 6. Exhaustion kinetics of (A) Polar Blue G (10) and (B) 1:2 metal complex dye (16) on untreated wool samples in dyeing with liposomes, the bilayer lipid concentration remaining constant (A) 4.0 mM and (B) 1.25 mM and varying the PC:CH molar ratios.

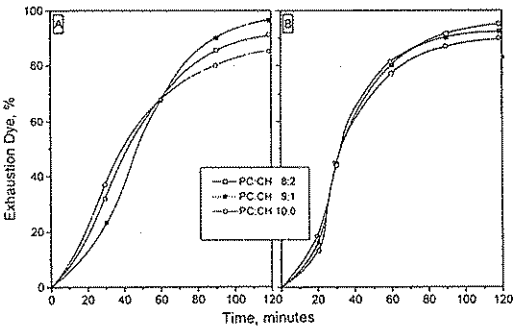

FIGURE 7. Exhaustion kinetics of (A) Polar Blue G (10) and (B) Acid Yellow 129 (16) on untreated wool samples by means of liposomes using only encapsulated dye, the bilayer lipid concentration remaining constant (A) 4.0mM and (B) 1.25 mM at different PC:CH molar ratios.

molar ratio of CH in these structures, the lower the inhibition of dye exhaustion.

This opposite behaviour may be correlated with the different chemical structure of these two types of dyes, which could affect both the assembly properties of dye-liposome systems and their hydrophobic interactions with the hydrophobic regions within the fibre, affecting the diffusion of dye into the fibre. In order to improve our understanding of these mechanisms a series of experiments were carried out based on liposome dyebath exhaustions using only the dye encapsulated in the liposomes.

Influence of encapsulation

Given that most of the dye molecules included in liposome suspensions are placed in the aqueous medium which surrounds the vesicles (maximum encapsulation efficiency of LUV liposomes of about 25%), we carried out a series of experiments, based on the liposome dyebath exhaustion, using only the dye encapsulated in the liposomic structures with acid milling dyes (7,9,10) and with 1:2 metal complex dyes (16). To this end, wool samples were treated with liposomes which contained the dyes after freeing the unencapsulated dye by separation through Sephadex G-50 resin. The PC:CH molar ratios varied from 10:0 to 8:2 and the total lipid concentration remained constant (Figure 7).

In the two cases, dye exhaustion kinetics shows different tendencies depending on the CH concentrations present in the bilayers. Thus, the initial dyeing phase shows an increasing inhibition of dye exhaustion, which reaches the maximum for the PC:CH molar ratio 9:1 for acid milling dyes and 8:2 for metal complex dyes. However, the final dye exhaustion appeares to be directly correlated with the CH present in bilayers, reaching the highest exhaustion for the same PC:CH molar ratios. It is interesting to note that in all cases the exahustion curves show an inflexion point. This means that this behaviour does not depend on the type of liposome or on the chemical structure of the dye used which may be attributed to the presence of CH in bilayers.

Comparison of dye exhaustion obtained with complete liposomes or using only the encapsulated dye (Figures 6 and 7) reveals that the inhibitory influence of CH in the initial dye exhaustion and the improved final dye exhaustion obtained using exclusively the encapsulated dye liposomes may confirm the role of the cell membrane complex (CMC) in the transport of dyestuffs given that the CMC presents a bilayer structuration which is similar to that of the liposomes (28-30).

D. Dye Bonding on Wool

In order to find out whether liposomes as dye carriers bring about changes to dye-wool fibre bonding forces after dyeing, successive extractions by pure ethanol and ammonia were performed on dyed samples via

LUV or MLV liposomes for the different dyes in the range of the lipid concentration studied (7-16). In general, the amounts of extracted dye via ammonia were clearly higher than those extracted using pure ethanol.

The amounts of extracted dye were inversely correlated with the lipid concentration of liposomes in all cases. Furthermore, increasing amounts of CH in bilayers led to a progressive diminution in the amounts of extracted dye regardless of the type of liposome used. The use of unilamellar or multilamellar bilayer structures does not seem to affect the total amount of extracted dye.

The overall evidence confirms the role of the CH in liposomes as effective carriers for bonding of milling acid dyes on wool fibres. This effect may be attributed to the fact that the CH affects the spontaneous release of encapsulated solutes and decreases the tendency of the vesicles to aggregate once they are formed. Likewise, the presence of CH in the CMC, could explain the role of this compound in the diffusion of the dye from the surface towards the centre of the fibre and in the improvement of the dye-fibre bonding forces in wool dyeing.

Figure 8 shows the amounts of bonded dye in wool fibres given as the difference between the amounts of adsorbed dye after dyeing and total extracted dye for Polar Blue G and Disperse Violet 1 dyes via MLV liposomes, versus lipid concentration (lipid compositions (PC:CH 10:0 and 8:2 molar ratio).

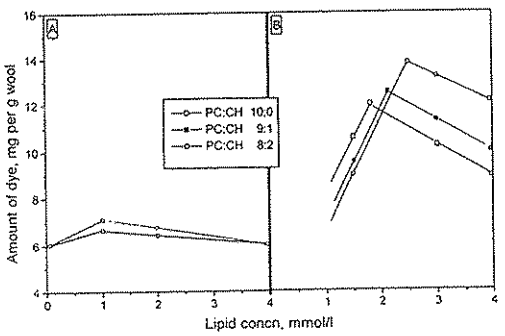

FIGURE 8. Amounts of bonded dye in wool fibres for (A) Polar Blue G (10) and (B) Disperse Violet 1 (13) via MLV liposomes versus lipid concentration for different levels of CH in bilayers

Eventhough the dye extraction is inversely related to the lipid concentration and the cholesterol amounts in the bilayers, the inhibitory effect of the lipids on the total dye adsorption is reflected in these figures in which an optimum of lipid composition is found in all cases. Therefore, a balance is reached between the inhibitory effect of the lipids especially at high lipid concentrations and the fixation effect of these vesicles.

In the light of our results we shall consider two major aspects related to the dyeing of wool fabrics via liposomes: Kinetics and bonding of dyes into the fibre.

Depending on both PC concentration and relative concentration PC:CH a variable inhibition of dye exhaustion during dyeing can be obtained. In fact, the function of levelling agents in a dyeing process is based on their regulatory action leading to an equilibrium between vehiculization of the dye to the fibre and the appropriate bonding in the keratinic structure. The special characteristics of liposome bilayers could encourage this levelling function; moreover, dye delivery by liposomes could be a versatile strategy for modulating the dyeing process in order to obtain a progressive dye exhaustion on the fibre with a suitable and durable dye bonding on the active sites of the keratinic structure. We postulate that the dye vehiculization by liposomes is as important as the lipidic pathways existing in the CMC realms.

E. Polyester Dyeing

Polyester is a synthetic fibre with a compact and crystalline structure. Polyester has a high glass transition temperature, approximately 80°C, and so dyeing with disperse dyes is done at high temperatures to achieve satisfactory dyeing rates. The use of carriers (phenols, amines, aromatic hydrocarbons, esters, etc.), accelerates the dyeing rate and allows dyeing at atmospheric pressure without reaching very high temperatures.

In our work we evaluated the effect of liposomes as carriers in polyester dyeing with disperse dyes. Given the complexity of the dyeing process only one type of liposome (Ecotrans-100-H) and one disperse dye (Terasil Yellow 4G) were used. Three variables were studied: amount of liposomes, amount of dye and different temperatures. Therefore, the dyeing series

were performed with 0.2 to 3% owf of dye, and 0.1 to 0.6% of PC owf, at temperatures ranging from 100°C to 120°C. Fifteen assays were planned according to a Box and Behnken experimental plan (31) for three variables (Table 1).

After dyeing the samples, dye bath exhaustion was determined and superficial dye was extracted with acetone. The internal percentage of dye bonded to the polyester fibres was determined by the difference between the dye exhausted (%) and the dye extracted (%). The numerical results obtained are listed in Table 1, and Figures 9 and 10 show the optimization contour lines of dye exhaustion, and internal bonded dye.

Dye exhaustion (Figure 9) and internal bonded dye (Figure 10) increase when temperature rises and the dye concentration decreases. As the temperature rises, the plasticizer action on polyester is more marked, the dye particles have more energy and movement. Furthermore, at low dye concentrations, they have more possibilities to be optimally fixed in the interior of the fibre.

The influence of liposomes on dye exhaustion is not dependent on the amount of dye and the temperature. There is a maximum in dye exhaustion when the dyebath contains 0.3% of PC o.w.f. Furthermore, the percentages of superficial dye extracted for polyester with acetone at low temperatures are closely related to the presence of liposomes. It should be pointed out that for the same temperature and same dye concentration, lower amounts of superficial dye were extracted at higher amounts of liposomes (see samples 1 and 3; 11 and 12, in Table 1). The liposome favours the diffusion of the dye at low temperatures since the superficial dye is minimum. This fact is reflected in a shift of the maximum of internal dye bonded to a 0.4% of PC owf shown in Figure 10.

Table 1. Percentage of dye exhaustion, dye extracted, and internal dye bonded after dyeing polyester via liposomes at different concentrations and different temperatures.

Samp N°	Temp °C	Dye % owf	PC % owf	Dye exh. %	Sup. dye ext. %	Dye bond %
1	100	1.6	0.1	69.19	24.07	45.12
2	120	1.6	0.1	99.43	0.96	98.47
3	100	1.6	0.6	67.65	8.21	59.44
4	120	1.6	0.6	99.33	0.91	98.42
5	100	0.2	0.35	100	9.32	90.68
6	120	0.2	0.35	100	6.00	94.00
7	100	3	0.35	26.44	25.49	0.95
8	120	3	0.35	99.08	0.78	98.3
9	110	0.2	0.1	100	6.69	93.31
10	110	0.2	0.6	97.37	6.52	90.85
11	110	3	0.1	51.45	9.49	41.96
12	110	3	0.6	41.76	1.9	39.86
13	110	1.6	0.35	81.63	2.21	79.42
14	110	1.6	0.35	87.65	2.46	85.19
15	110	1.6	0.35	90	1.74	88.26

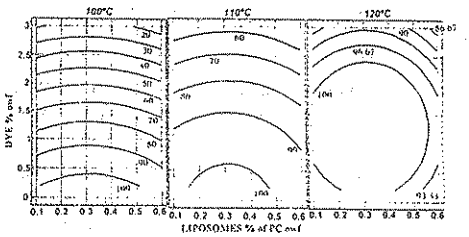

Figure 9. Contour line of dyebath exhaustion of terasil Yellow 4G on polyester samples in dyeing with liposomes.

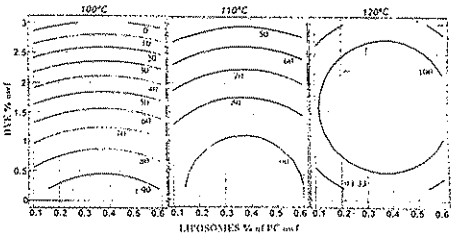

Figure 10. Contour line of total bonded dye to polyester samples in dyeing with liposomes.

The influence of liposome regardless of the dye concentration is worth noting. This implies an action mechanism of the vesicles more directly related to the polyester fibre than to the disperse dyes. Therefore, this optimum found at the maximum internal bonded dye regardless of the dye concentration and temperature enables us to fix the liposome amount to a 0.4% of PC owf for the next experiments.

F. Polyester/Wool Blend Dyeing

Although wool/polyester blends are industrially dyed with polyester dyes and wool dyes together, this study is focused on the use of disperse dyes and their interaction with vesicles formed by environmentally harmless biological lipids.

Liposome action on polyester/wool blend dyeing was studied using the same liposome and disperse dye as before, including polyester fabric and a wool fabric in the same bath. This allowed us to determine not only dye exhaustion but also dye fixation on each fibre.

Since the amount of liposome has already been fixed (0.4% of PC owf), two variables were studied, dye concentration (0.2 to 3% owf) and temperature (100 to 120°C). Eleven assays were again planned according to the Box and Behnken (31) experimental plan for two variables using the experimental conditions listed in Table 2.

The same experiments were also performed with conventional auxiliaries, (Optinol BD 1.5g/l and Tanacid TAB 0.8 g/l) and without any auxiliary product for comparison with the liposome experiments (Table 3 and Table 4). After dyeing, dyebath exhaustion was determined, superficial dye was extracted from polyester with acetone and non bonded superficial and internal dyes were extracted from wool with ethanol and ammonia, respectively.

An approximation of total dye bonded was calculated by the difference between the dye exhausted (%) and the dye extracted from polyester and wool (%). All numerical results are listed on Tables 2-4 and the optimisation contour lines are shown in Figures 11 and 12.

Comparison of the contour lines of exhaustion of polyester/wool blend dyeing using liposomes, conventional carrier or without auxiliaries (Figure 11),

Table 2. Percentage of dye exhaustion, dye extracted and total dye bonded, after dyeing of polyester/wool blends with liposome (0.4% of PC o.w.f.) at different dye concentrations and different temperatures.

Samp N°	Temp °C	Dye % owf	Dye exh. %	Sup. dye ext. PES %	Dye ext. WO %	Dye bond %
1	100	0.2	98.18	23.47	8.89	65.82
2	100	1.6	75.45	4.19	1.76	69.5
3	100	3	31.8	27.17	2.44	2.19
4	110	0.2	98.66	14.98	4.37	79.61
5	110	1.6	98.64	3.74	1.48	93.42
6	110	3	40.88	17.39	1.98	21.51
7	120	0.2	100	10.9	7.55	81.55
8	120	1.6	99.22	1.11	0.32	97.79
9	120	3	62.91	2.83	1.47	58.61
10	110	1.6	98.19	2.13	1.22	94.84
11	110	1.6	100	2.5	0.99	96.51

Table 3. Percentage of dye exhaustion, dye extracted and total dye bonded after dyeing of polyester/wool blends with a carrier (1.5 g/l) and a dyeing auxiliary (0.8 g/l) at different dye concentrations and different temperatures.

Samp N°	Temp °C	Dye % owf	Dye exh. %	Sup. dye ext. PES %	Dye ext. WO %	Dye bond %
1	100	0.2	97.45	14.77	23.08	59.6
2	100	1.6	90.04	8.4	22.18	59.46
3	100	3	67.15	21.81	9.47	35.87
4	110	0.2	100	13.22	16.44	70.34
5	110	1.6	97.56	9.09	20.92	67.55
6	110	3	87.03	16.9	3.03	67.91
7	120	0.2	100	8.01	9.04	82.95
8	120	1.6	99.7	2.89	10.58	86.23
9	120	3	99.61	1.3	6.99	91.32
10	110	1.6	98.06	11.71	25.55	60.8
11	110	1.6	97.16	12.02	28.92	56.22

Table 4. Percentage of dye exhaustion, dye extracted and total dye bonded after dyeing of polyester/wool blends without any dyeing auxiliary at different dye concentrations and different temperatures.

Samp N°	Temp °C	Dye % owf	Dye exh. %	Sup. dye ext. PES %	Dye ext. WO %	Dye bond %
1	100	0.2	86.96	38.07	47.42	1.47
2	100	1.6	59.63	16.11	26.96	16.56
3	100	3	49.38	21.94	11.18	16.26
4	110	0.2	95.24	24.03	28.64	42.57
5	110	1.6	91.94	6.26	9.37	76.31
6	110	3	99.68	8.27	5.17	86.24
7	120	0.2	95.24	8.18	17.86	69.2
8	120	1.6	99.68	0.96	12.08	86.64
9	120	3	61.63	3.81	12.13	45.69
10	110	1.6	90.74	6.65	5.89	78.2
11	110	1.6	84.78	2.92	5.58	76.28

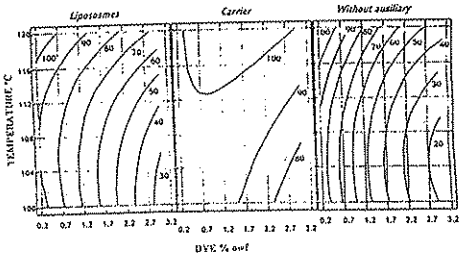

Figure 11. Contour line of bath exhaustion of Terasyl Yellow 4G on polyester/wool blend samples in dyeing with liposomes, using carrier or without using any dyeing auxiliary.

shows that to achieve the same dye exhaustion close to 100% obtained with Optinol, a low concentration of dye and a high temperature are necessary. However, the comparison without any dyeing auxiliary allows us

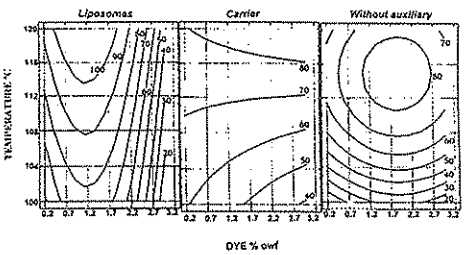

Figure 12. Contour line of total amounts of bonded dye on polyester/wool blend samples in dyeing with liposomes, using carrier or without using any dyeing auxiliary.

to appreciate the effect of liposomes, which shows a 15% increase in dye exhaustion.

Acetone extractions of dyed polyester samples via liposomes showed, in general, smaller values than those obtained from samples dyed without liposomes (using a carrier or without any dyeing auxiliary). These results confirm the role of liposomes in dyeing inducing the penetration of disperse dyes on polyester fibres.

Likewise, the values of dye extracted obtained for wool fibres are much lower when the liposomes are present in the dye bath. The percentage values of dye extracted from wool are always below 10% (Table 2) whereas they are mostly above 10% in Tables 3 and 4. Therefore, it can be concluded that disperse Terasil dye is more bonded on polyester and especially on wool when the dyeing is carried out in the presence of liposomes.

Since the total dye bonded is obtained by the difference between dye exhaustion and the dye extracted on the two fibres, and since the liposomes have improved fixation on both fibres, the total bonded dye on polyester and wool samples are similar and in some cases exceed those for the conventional dyeing with a carrier and for the dyeing without any dyeing auxiliary. The contour lines of total bonded dye on polyester/wool blends treated differently are shown in Figure 12. The higher amount of bonded dye with liposomes with respect to the dyeing without a dyeing auxiliary (30% superior) should be noted. Even though the presence of a carrier leads to a maximum bonded dye of 80% at temperatures higher than 115°C, the presence of liposomes leads to a 100% bonded dye at temperatures higher than 115°C but only at low dye concentrations.

In the light of these assays it may be deduced that the effect of liposomes improves dye exhaustion and that dye fixation is able to compete with conventional carriers with light shades.

CONCLUSIONS

From our findings, we conclude that a new method of wool dyeing by means of liposomes may be considered suitable for modulating the dye exhaustion of commercial milling acid dyes, disperse dyes and metal complex dyes, thereby increasing the dye bonding in untreated wool fibers.

LUV and MLV liposome suspensions at pH 5.5 are physicochemically stable during the dyeing process for both dyes studied, the bilayer lipid concentration ranging from 0.5 to 4.0 mM. The presence of increasing amounts of CH in liposomes improves the stability of these structures for both particle size distribution and polydispersity index.

The inhibition of dye exhaustion of untreated wool fabrics is directly dependent on both the liposome lipid concentration and the structure of liposomes. The use of LUV liposome structures results in a greater decrease in dye exhaustion compared with the use of MLV liposomes. This inhibition is also directly dependent on the CH concentration in bilayers, especially for the initial and final stages of dyeing. The exclusive use of the encapsulated dye brings about changes in the dyeing kinetics. Thus, although initially the dye exhaustion is inhibited, the final dye exhaustion rises with the CH concentration in bilayers. The control of dye exhaustion allows modulation of dye adsorption on wool fibres, thereby improving both regularity and homogeneity of the dye adsorption and bonding on untreated wool fibers. Given that this control is especially important in the initial dyeing stages, (where excessive dye adsorption leads to staining irregularities), the bilayer lipid concentration and particularly the PC:CH ratio could act as a specific levelling mechanism for each dye.

As for the bonding of dyes in wool fibers, despite the aforementioned inhibition of dye exhaustion, the increasing concentrations of lipids in the bilayers enhance the percentage of bonded dye into the fibres.

This tendency is also observed when the CH concentration in bilayers is increased.

The importance of the role played by liposomes in wool dyeing was demonstrated taking into account both the dyeing modulation and the strategic biomimetic aspects. It is reasonable to predict that an optimization of experimental conditions of dyeing using liposomes could be obtained thereby improving additionally fastness of wool dyed samples. Some other liposome strategies could be applied to wool processing taking into consideration the special lipo-keratinic structure of wool fibers, in particular the existence of lipids in the Cell Membrane Complex.

The carrier character of liposomes was demonstrated, leading to dye exhaustion and fixation under some optimum experimental conditions in the dyeing of polyester with disperse dyes. This exhaustion is dependent on the liposome/fibre ratio in the dyebath regardless of the dye concentration and temperature.

Liposomes action was valued in blends of polyester/wool with disperse dyes in optimum conditions for polyester dyeing. In this case dyebath exhaustion depended on the dye concentration, obtaining higher exhaustion levels at higher temperatures and with only light shades. The dye bonded on polyester and wool was higher with liposome dyeing than with commercial carrier dyeing.

The role played by liposomes in polyester/wool dyeing using disperse dyes is worth noting. New strategies for wool/polyester blend dyeing could be devised using more specific biomimetic systems with a vesicular character prepared for textile applications.

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REFERENCES

1. Barni, E., Carpignano, R., Di Modica, G., Savarino, P., and Viscardi, G. 1988. *J. Disper. Sci. Technol.* **9**, 75-87.
2. Carrión, F.J. 1995. *Textile Res. J.* **65**, 362-368.
3. Kim, I.S., Kono, K., and Takagishi, T. *Textile Res. J.* In press.
4. Kim, I.S., Kono, K., and Takagishi, T. *Textile Res. J.* Submitted.
5. De la Maza, A., Parra, J.L., Bosch, P. 1991. *Textile Res. J.* **61**, 357-362.
6. De la Maza, A., Parra, J.L. 1993. *Textile Res. J.* **63**, 44-50.
7. De la Maza, A., Parra, J.L., Bosch, P., and Coderch, L. 1992. *Textile Res. J.* **62**, 406-413.
8. De la Maza, A., Parra, J.L., Manich, A.M., and Coderch, L. 1992. *J. Soc. Dyers Colour.* **108**, 540-545.
9. De la Maza, A., Parra, J.L. and Manich, A.M. 1993. *Textile Res. J.* **63**, 643-649.
10. De la Maza, A., Coderch, L., Manich, A.M., Bosch, P., and Parra, J.L. 1996. *Handbook of Nonmedical Applications of Liposomes*, edited by Lasic, D.D. and Barenholz, Y.Boca Raton, Florida:CRC Press, Inc.,p. 165-182.
11. De la Maza, A. and Parra, J.L. 1994. *Textile Res. J.* **64**, 255-261.
12. De la Maza, A. and Parra, J.L. 1994. *J. Soc. Dyers Colour.* **110**, 64-68.
13. De la Maza, A., Parra, J.L., Coderch, L., and Bosch, P. 1995. *J. Soc. Dyers Colour.* **111**, 30-35.
14. De la Maza, A., Manich, A.M., Coderch, L., and Parra, J.L. 1995. *Textile Res. J.* **65**, 163-170.
15. De la Maza, A., Coderch, L., Serra, S. and Parra, J.L., *J. Soc. Dyers Colour.* Submitted.
16. De la Maza, A., Coderch, L., Manich, A.M., Serra, S. and Parra, J.L., *Textile Res. J.* Submitted.
17. Martí, M., Coderch, L., De la Maza, A., Manich, A.M. and Parra, J.L., *Textile Res. J.* Submitted.
18. Singleton, W.S., Gray, M.S., Brown, M.L. and White, J.L., 1965. *J. Amer. Oil Chem. Soc.*, **42**, 53.
19. Paternostre, M.T., Roux M. and Rigaud, J.L. 1988. *Biochemistry*, **27**, 2668.
20. Rigaud J.L., Bluzat, A. and Buschlen, S. 1983. *Biochem. Biophys. Res. Commun.* **111**, 373.
21. Szoka, F., Olson, F. Heath, T. Vail, W.

Mayhew E. and Papahadjopoulos, D. 1980. *Biochim. Biophys. Acta* **601**, 559.
22. Bangham, A.D., Standish M.M. and Watking, J.C. 1965. *J. Mol. Biol.* **13**, 238.
23. Weinstein, J.N., Ralston, E., Leserman, L.D., Klausner, R.D., Dragsten, P., Henkart, P and Blumenthal, 1986. *Liposome Technology*, Gregoriadis G., Ed, CRC. Press Inc. Boca Raton, Florida,, Vol III, Chap 13.
24. Lichtenberg, D., Robson J. and Dennis, E.A., 1983. *Biochim. Biophys. Acta* **737**, 285.
25. Trotman, E.R., 1984. *Dyeing and Chemical Technology of Textile Fibres,* Charles Griffin and Company Ltd. Ed., England, , a) Chapter 12, b) Chapter 21.
26. Scherphof, G.L., Damen J. and Wilschut, J. 1986. *Liposome Technology* Gregoriadis, G. Ed, CRC Press, Inc. Boca Raton, Florida, Vol III, Chapter 14.
27. Deamer, D.W. and Uster, P.S., 1983. *Liposomes*, Ostro M.J. Ed, Marcel Dekker Inc. New York , Chapter 1.
28. Rivett, D.E., 1991. *Wool Science Rev.* **67**, 1.
29. Nogués, B., Coderch, L., Juliá, R., and Erra, P. 1988. *Textile Res. J.* **58**, 338-342.
30. Coderch, L., de la Maza, A., Pinazo, A. and Parra, J.L. 1996. *J. Am. Oil Chem. Soc.* **139,** 197-203.
31. Box, G.E.P. and Behnken, D.W. 1960. *Technometrics* Vol. 2 N°4.